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Ion beam and plasma technology development for surface modification at Los Alamos National Laboratory

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Abstract

We are developing two high-throughput technologies for materials modification. The first is a repetitive intense ion beam source for materials modification through rapid surface melt and resolidification (up to 10^{10} K s^{-1} cooling rates) and for ablative deposition of coatings. The short range of the ions (typically 0.1 to 10 μm) allows vaporization or melting at moderate beam energy density (typically 1–50 J cm^{-2}). A new repetitive intense ion beam accelerator called CHAMP is under development at Los Alamos. The design beam parameters are: $E = 200$–250 keV, $I = 15$ kA, $\tau = 1$ μs, and 1 Hz. This accelerator will enable applications such as film deposition, alloying and mixing, cleaning and polishing, corrosion and wear resistance, polymer surface treatments, and nanophase powder synthesis. The second technology is plasma source ion implantation (PSII) using plasmas generated from both gas phase (using radio frequency excitation) and solid phase (using a cathodic arc) sources. We have used PSII to directly implant ions for surface modification and as a method for generating graded interfaces to enhance the adhesion of surface coatings. Surfaces with areas of up to 16 m^2 and weighing more than a thousand kilograms have been treated in the Los Alamos PSII chamber. In addition, PSII in combination with cathodic source deposition has been used to form highly adherent, thick Er_2O_3 coatings on steel for reactive metal containment in casting. These coatings resist delamination under extreme mechanical and thermal stress.

Keywords: Plasma; Implantation; Ion beams; Ions; Coatings; Surface treatment

1. Introduction

At Los Alamos National Laboratory, we are developing two high-throughput, low-cost technologies for treating materials. The first, intense ion beam technology, used as a flash heat source for surface treatment and ablative coatings, has been demonstrated for a number of applications in single shot experiments. In the first part of this paper, we describe the development of a new ion beam accelerator to produce more controlled and reproducible beams than are currently available. This accelerator can be repetitively fired for commercial application. In the second part of the paper, we describe plasma source ion implantation technology (PSII) that takes the known advantages of ion implantation and makes them available for the treatment of large-area complex components. PSII is also used to make graded interfaces to improve the adherence of coatings on substrates. The process for making shock resistant erbia coatings is described in detail.

2. Intense ion beam technology

Over the past decade, researchers in Japan, Russia and the United States have been investigating the application of intense-pulsed-ion beam (IPIB) technology, with roots in inertial confinement fusion programs, to the surface treatment and coating of materials. The short range (0.1–10 μm) and high-energy density (1–50 J cm^{-2}) of these short-pulsed ($\tau \leq 1$ μs) beams (with ion currents $I = 5$–50 kA, and energies $E = 100$–1000 keV) make them ideal flash-heat sources to rapidly vaporize or melt the near surface layer of targets, similar to the more familiar pulsed laser deposition (PLD) or laser surface treatment. The vaporized material can form coatings on substrates, and surface melting followed by rapid cooling (10^{10} K s^{-1}) can form amorphous layers, dissolve precipitates, and form non-equilibrium microstructures [1,2].

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An advantage of this approach over laser processing is that these beams deliver 0.1–10 kJ per pulse to targets at expected overall electrical efficiencies (i.e. the ratio of extracted ion beam energy to the total energy consumed in generating the beam) of 20%–40% (compared with $<1\%$ for the excimer lasers often used for similar applications). Consequently, IPIB hardware can be compact and require relatively low capital investment. This opens the promise of environmentally conscious, low-cost, high-throughput manufacturing. Further, excellent coupling of incident ion energy to targets is achieved, as opposed to lasers that may have limited coupling to reflective materials, or produce reflecting plasmas at high incident fluence. The ion range is adjustable through a selection of the ion species and kinetic energy, and the beam energy density can be tailored through the control of the beam footprint at the target to melt (1–10 J cm^{-2}) or to vaporize (10–50 J cm^{-2}) the target surface. Beam pulse durations are short (≤ 1 μs) to minimize thermal conduction. Some disadvantages of IPIB processing over laser processing include the need to form and propagate the beams in vacuum, and the need for shielding of X-rays, which are produced by a relatively low-level electron current also present in IPIB accelerators. Also, these beams cannot be as tightly focused on to targets as lasers making them unsuitable for applications requiring selective treatment on small spatial scales. Applications investigated have included film deposition, alloying and mixing, glazing, cleaning and polishing, corrosion and wear resistance, implantation and annealing, polymer surface treatment, and nanophase powder synthesis.

Beams are produced in vacuum by magnetically insulated diodes requiring a source of ions, an accelerating voltage, and a magnetic field transverse to the acceleration gap to suppress electron flow and enhance the ion flow. Ion currents typically exceed the vacuum space-charge limit by 5–50 times owing to electrons confined in the acceleration region by the applied magnetic field. The beams are produced and transported in vacuum below 10^{-4} Torr. In a conventional diode, ions are drawn from the surface of a polymer anode converted to a plasma by a combination of high-voltage flashover and electron impact. Polymer anodes are unacceptable for many materials synthesis applications because of their limited lifetime, excessive heat loading, high gas production, excessive debris, poor beam uniformity, and lack of ion species control. Anodes that draw ions from a preformed plasma are being developed at a number of laboratories to overcome the above limitations. Traditional single-shot beam accelerators (using Marx generators and high-voltage pulse lines), incompatible with low-cost high-throughput commercial processing, are yielding to new high-average-power accelerators. At Los Alamos we are developing a repetitive beam accelerator called CHAMP (Continuous High Average-power Microsecond Pulser). This system, which uses lumped element transmission lines and high-power thyratron switches, is being developed to generate a sequence of 1 μs pulses.

The CHAMP accelerator will use a magnetically insulated extraction diode (see Fig. 1) with the plasma anode in a ballistically focused geometry (45° full focusing angle with a 30 cm focal length). The anode consists of a flat pulsed induction coil in an aluminum housing. The high-voltage coil is formed from four parallel sets of two turn spiral windings coaxial with the system axis. The coil in focusing geometry is dished in the form of a cone having a normal to the surface of 22.5° with respect to the system axis. The diode operates as follows. The plasma anode is formed by first radially ducting a puff of gas with a fast acting valve (risetime ~ 100 μs), located on axis, over the coil surface. The valve is actuated by a metallic diaphragm driven either by eddy currents or a voice–coil mechanism. When the gas puff is properly distributed, a fast rising current pulse (10–20 kA, $\tau_{rise} = 1$ μs), delivered to the induction coil breaks down the gas and induces an azimuthal current in the plasma at the coil surface. The $j_\theta \times B_r$ force on the plasma accelerates the plasma to the radial opening in the aluminum anode housing where it is stagnated against the applied radial magnetic field and where ions can be extracted. The cathode consists of the tips of two thin concentric metal conical sections (or cylinders for unfocused geometry). The gap between the cathode tips and the plasma anode is 2 cm. Just before the application of the accelerating voltage, a 200 μs risetime magnetic field of about 2 kG is applied transverse to the anode–cathode gap by two magnetic field coils—one located inside the inner cone and one located outside the outer cone. At peak field and when the plasma is in position at the anode housing aperture, a positive accelerating voltage pulse supplied from a high-voltage modulator is applied to the anode. The applied magnetic field strength is adjusted to prevent electrons from crossing the anode–cathode gap, but the more massive ions, only very weakly deflected by the magnetic field, have approximately linear trajectories. The insulating transverse magnetic field ($B \sim 2\, B_{crit}$, where B_{crit} is the minimum field for insulation of the electrons given by the condition that the electron gyroradius equals the anode–cathode gap) will be generated by the two magnetic field coils on the grounded cathode focusing cones. The expected beam parameters are $E = 200$–250 keV, $I = 15$ kA, and $\tau = 1$ μs.

The beam electrical system requires many modulator subsystems synchronized with each other and the ion acceleration pulse (Fig. 2). A gas puff modulator and the induction coil modulator sub-system will be housed in a 'hotdeck' chassis at a common potential with the pulsed anode. For electrical isolation, fiber optic cables will carry fast control and diagnostic signals. Solid-state switches will be used to deliver the current from storage capacitors to the magnetic field coils at ground potential. A dedicated fast sequence and monitor system will confirm the proper sub-system parameters before the main diode discharge is initiated to minimize damage to components in case of off-normal operation. The accelerating power system will utilize four parallel type 'E' Blumlein lines each switched with an English Electric Valve CX1736AX thyratron. The number of networks comprising each Blum-

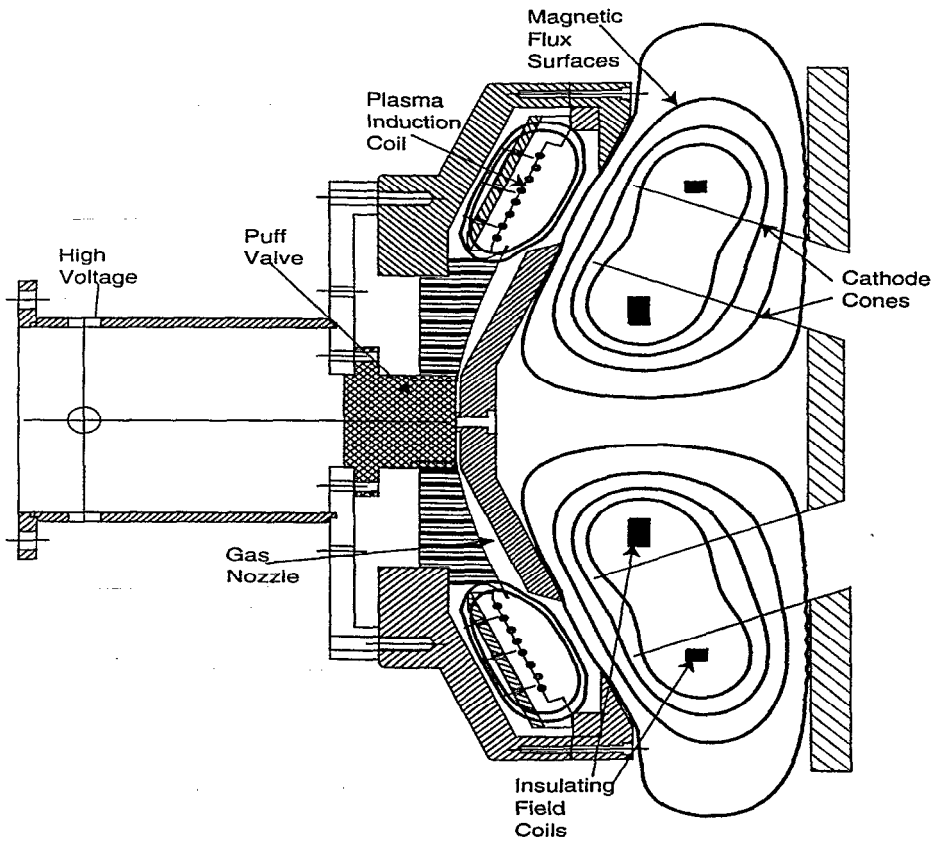

Fig. 1. Magnetically insulated diode with plasma anode.

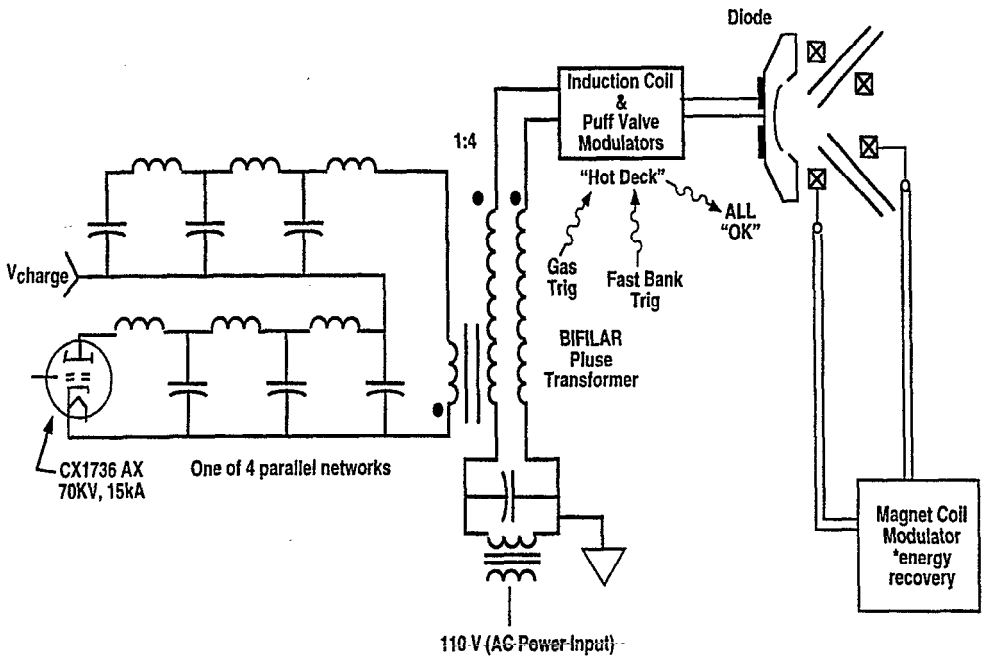

Fig. 2. CHAMP circuit.

lein line will depend on the pulse fidelity required by each application. For materials applications, square voltage and current waveforms are not desired since a spread in ion energy leads to a more uniform deposition profile in targets (this eliminates the Bragg peak near the end of the ion range produced by a monoenergetic beam).

The accelerator power system will be housed in a metal tank approximately 2 m × 2 m × 2 m. The initial system will

use recycled capacitors for the Blumlein lines to minimize development cost. With higher energy density state-of-the-art capacitors the modulator footprint could be reduced significantly. The modulator tank will be filled with a high-voltage transformer oil. Estimates of the electrical efficiency give 30% ± 10%, including power to make the plasma and the pulsed magnetic field.

The status of the CHAMP project is as follows. The cathode and anode hardware, and vacuum system have been fabricated. The induction coil and gas drivers have also been fabricated and tested. Anode plasmas have been produced and their properties are currently being measured. The transformer and thyratron driver circuits have been purchased, and the beam acceleration power system is being fabricated. Magnetic field coils capable of repetitive firing have been designed. Operation of the accelerator is expected during 1998.

3. Large area plasma source ion implantation

PSII is a non-line-of-sight technique for ion implantation over large surface areas and objects of complicated shape [3]. In PSII (Fig. 3), an object is placed in a plasma containing the ion species to be implanted, and then pulse biased to a high negative potential, accelerating the plasma ions through an electron-depleted sheath region and implanting them in the surface. Its primary advantage over conventional ion beam implantation is that manipulation of the object and rastering of the beam for uniform coverage are not necessary. In this way, very large objects can be implanted with relative ease. In the CTX PSII Facility at Los Alamos National Laboratory, objects with areas of 16 m^2 and weights of more than a ton have been treated [4,5]. The plasma from which the ions are derived can be produced by a variety of methods—common methods include capacitively or inductively coupled radio frequency sources for gaseous species, and cathodic-arc sources for metal ion species, although such arc sources tend to be inherently line-of-sight.

The primary PSII facility at Los Alamos [6] uses a cylindrical plasma processing chamber 1.5 m in diameter by 4.6 m long. Implantation (or DLC Deposition) can be powered by one of several available switching supplies. Typical implantation operating conditions of 13 to 40 mPa (neutral gas fill pressure), and radio frequency (RF) power from 100 to 1000 W, result in plasma densities ranging from 10^{14} to 10^{16} m^{-3}, with uniformity to better than 10% over the bulk of the chamber.

4. Functionally graded interfaces

Although PSII has proven useful for 'pure' ion implantation applications such as nitrogen implantation of aluminum, chromium, and titanium alloys, another important application is to use PSII as an adhesion-promoting pretreatment for a

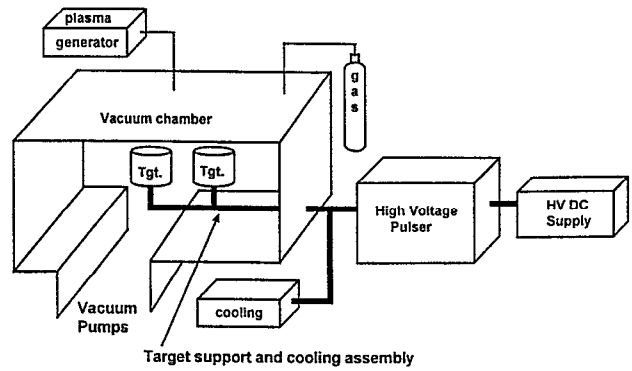

Fig. 3. Plasma source ion implantation configuration.

coating process. This multistep process has been used at Los Alamos to produce thick (up to 10 μm) coatings of diamond-like carbon (DLC) on aluminum [7,8] and steel [9], and boron carbide on silicon and molybdenum [10].

Coatings of erbia and other rare earth oxides are of interest for the containment of reactive molten metals in casting operations because these oxides have very high melting and boiling points, low vapor pressures at elevated temperatures, large negative free energies of formation. This latter property means that they cannot be reduced by the molten metal, making them impervious to attack, and, in many cases, non-wetting. However, it is difficult to make these brittle ceramic materials adhere to metal substrates, particularly under conditions of mechanical or thermal shock. At Los Alamos, the PSII process has been used to create highly adherent coatings of erbia (erbium oxide, Er_2O_3) on a variety of substrates including steel, tantalum, molybdenum, silicon, aluminum, and niobium. Such coatings on steel have been demonstrated to survive casting operations involving temperatures above 1000°C and thermal shock resulting from molten metal being poured on to relatively 'cold' coatings.

To produce these highly adherent coatings, a cathodic-arc, shown in Fig. 4, is utilized as a plasma source. This arc source, and the solid-state arc pulse modulator that drives it have been described in detail elsewhere [11], as has the high

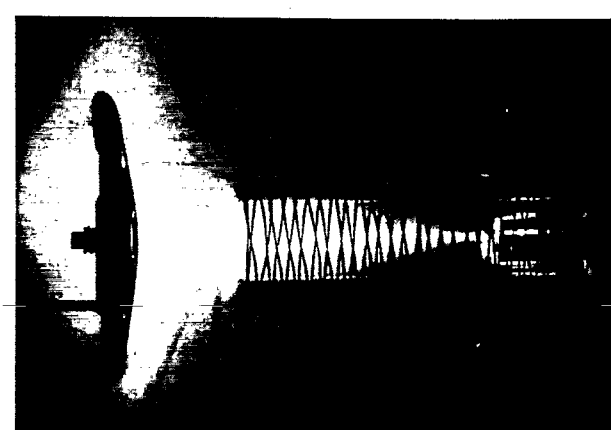

Fig. 4. Cathodic-arc with linear macroparticle filter used to deposit erbia coatings.

voltage pulse modulator which supplies the 20 μs, 20 kV implantation bias pulses to the substrate being treated. The standard erbia 'recipe' developed at Los Alamos involves a sputter cleaning step, two implantation steps, and a deposition step. The initial argon sputter cleaning, utilizing a −500 V self-bias resulting from a 13.56 MHz r.f. signal applied to the substrate, removes surface oxides and adsorbed gases and water. The first implantation step is a 'pure' implantation, utilizing plasma pulses and target bias pulses, which are synchronized and of approximately the same duration (a few tens of microseconds), so that all the ions are implanted at near the full applied bias voltage. Because the erbium ions are typically charged +2 and +3, implantation energies of 40 keV and 60 keV result from the applied −20 kV substrate bias. Achieving an energetic implantation can be important for producing a functionally graded interface when working with heavy metal ions, since the implantation depths are shallow, and the implantation retained dose saturates at a low level due to surface sputtering. This synchronized mode of operation and its implications for substrate bias, modulator load and ion implantation energy have been described elsewhere [12,13]. In the second implantation step, the plasma pulse is lengthened to a few hundred microseconds, while maintaining the high voltage target bias pulses, and bleeding in a low background pressure (about 0.1 mTorr) of oxygen. This results in the simultaneous implantation and deposition of an oxide layer about 100 nm thick. In the deposition step, the high voltage target bias is replaced by a pulsed −500 V target bias, and the plasma production pulses are lengthened as much as needed to achieve the desired deposition rate and coating thickness. A linear magnetic filter, constructed by wrapping a solenoid in series with the arc current around a Pyrex tube, as shown in Fig. 4, is often used during this step to reduce the flux of neutral macroparticles that are incorporated into the coating. As can be seen in the unfiltered coating shown in Fig. 5, such macroparticles can create a 'plasma shadow', resulting in a localized thin spot in the coating.

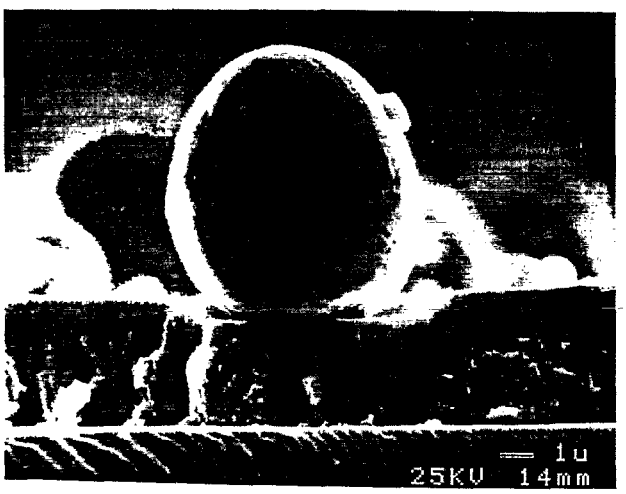

Fig. 5. Macroparticle on an erbia coating.

X-ray photoelectron spectroscopy (XPS) depth profiles were obtained of an erbia implant into 304L stainless steel produced from the process described above, but without the deposition step. The concentration depth profiles are shown in Fig. 6. The profiles clearly show a smooth transition from the underlying steel into the erbia coating, over a region approximately 20 nm in width. There is apparent diffusion of iron and chromium into the oxide coating. The depth profile also indicates the presence of erbium and oxygen beneath the steel surface and is indicative of the high-voltage implantation of these elements during one of the steps in the process.

An example of the high adherence achievable with this process can be seen in Fig. 7, showing an SEM image of a 3 μm erbia coating implanted and deposited on the inside of a shallow 304L stainless steel cup, which has subsequently been dented inside out with a 16 mm diameter Charpy Impactor. The erbia coating has cracked owing to the tensile stresses imposed by the deformation of the substrate, but has not delaminated. Such a cracked coating is still useful for containing reactive molten metals because surface tension inhibits its penetration of the molten metal through the erbia coating.

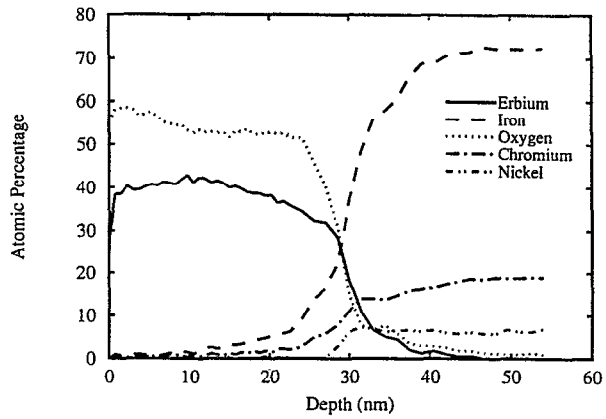

Fig. 6. XPS depth profile of an erbia–steel interface.

Fig. 7. A 3 μm erbia coating on 304L SS, which has been dented inside out with a Charpy Impactor. No delamination is observed.

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